Biodegradable Polymers. XI. Spectral, Thermal, Morphological, and Biodegradability Properties of Environment-Friendly Green Plastics of Soy Protein Modified with Thiosemicarbazide

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ABSTRACT: The demand for biodegradable polymers produced from renewable natural resources continues to grow as environmental concerns increase. Biodegradable plastics derived from agricultural feedstock are a new generation of materials capable of reducing the environmental impact in terms of energy consumption and greenhouse effect in specific applications to perform as traditional/conventional plastics when in use and are completely biodegradable within a composting cycle through the action of living/micro-organisms. The objective of this study is to examine the potentiality and performance pattern of soy protein isolate (SPI) resin, modified with various concentrations of thiosemicarbazide (TSC), as a thermoplastic to substitute some conventional petroleum-based plastics. The spectral, thermal, morphological properties and the biodegradability of the modified resin have been investigated. The spectral studies indicate that TSC is not cross-linked with the protein moiety; rather, it acts as a modifier. Thermogravimetric analysis of the modified material has been followed using a computer analysis method (LOTUS package) developed by us for assigning the degradation mechanism. A number of equations have been used to evaluate the kinetic parameters. The degradation mechanism has been ascertained on the basis of the kinetic parameters. It is expected that, this environment-friendly, fully biodegradable and sustainable TSC-modified SPI green plastic could be commercially used for making molded products. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3134–3142, 2007

Key words: biodegradable; modification; thermogravimetric analysis; differential scanning calorimetry

INTRODUCTION

Sustainability, industrial ecology, eco-efficiency, and green chemistry are the new principles that are guiding the development of next generation of plastic and other products and processes. Thus, new products have to be designed and engineered from ''conception to reincarnation'' incorporating a holistic ''life cycle thinking approach.'' The rational and drivers for manufacturing eco-efficient, sustainable, and biodegradable/compostable plastics are now being discussed on the basis of global carbon recycling, design principles for the environment, and disposal/waste management infrastructures. Designing plastics, used in single-use disposal packaging and consumer goods, to be biodegradable and ensuring that they end up in a composting system is environmentally and ecologically sound. Composting is an economically important tool, not only for waste management but also for sustainable agricultural practices. Biodegradable plastics and bio-based products based on annually renewable agricultural- and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock.[1–9]

Out of all agricultural products, soy protein polymers have been recently considered as an alternative to reduce the use of petroleum-based polymers for various commercial applications and reduce environmental pollution.[10–16] Soy protein consists of soy isolate, soy concentrate, and soy flour. Among the soy proteins, soy protein isolate has been extensively studied because of its high protein content and purity, easy availability, low cost, and biodegradability. The protein content of soy protein isolate (SPI) is more than 90% and is higher than that of other soy protein products such as soy protein concentrate and soy flour. The proteins have a wide range of molecular

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weight of 8 kDa to about 600 kDa. The various components are identified as 2S, 7S, 11 S, and 15S (Svedberg's unit), and usually found in the 20–22, 37, 31–40, and 10–11 range (of total weight) in the SPI, respectively,.[17] Hence 7S, and 11S, α-glycine (42–58 kDa), and glycine (360 kDa) are the two major globulins present in SPI. The proteins can react with each other to form various crosslinkages such as disulphide, lysinoalanine, and lanthionine. The 11S component forms more disulphide links than the 7S component.[18] The resin obtained from unmodified SPI is very brittle and hence inconvenient for processing. Hence modifiers/plasticizers are required to make it flexible/processable for making finished products. Studies by various authors have shown that soy proteins can be modified under high pressure to increase the hydrophobic properties.[19] Heat treatments have shown to reducewater vapor permeability and increase tensile strength.[20] Water resistance and tensile properties of soy protein films can be increased with crosslinking reactions and decreased by increasing processing temperature above decomposition temperatures.[21] Chemical modifications of soy protein have been studied by various authors to modify its properties.[18,22-24] Modifying SPI resin with stearic acid was successful in obtaining better tensile and thermal properties as well as reduced moisture sensitivity without any processing problems.[25]

Jane and coworkers[26] have patented a process for preparing molded thermoplastic articles using soy protein, where proteins, along with high temperature and pressure, are used to extrude solid articles as well as films. Modification of SPIs allows formed-biopolymers to approach the properties of synthetic polymers. Brandenburg[27] predicted that acetylation process reduces the water vapor permeability of soy protein films. Shalaby[28] has developed a special soy protein formulation and production process to make commercial soy-based products. Recently, Swain et al.[4–6] have used furfural, a bio-based aldehyde, to crosslink soy protein to modify its properties. These studies over the years have suggested that, soy protein could supplant other polymers when processed correctly using proper modifier or crosslinker or plasticizer.

Recently, we have communicated the uses of thiourea, semicarbazide, and urea as modifiers to enhance the properties of SPI for better plastic values.[7–9] In the present research program, we wish to report the spectral, thermal, and morphological properties along with biodegradability of thiosemicarbazide-modified SPI for various commercial applications.

EXPERIMENTAL

Materials

Soy protein isolate (SPI) with protein content of about 90% was obtained from Archer Daniels, Midland Co., (Decatur, IL) as a gift sample and used for the reaction. Thiosemicarbazide (TSC) and propionic acid were of reagent grade (GR) chemicals and used without further purification for modifying the protein.

TSC, CH_5N_3S, (1-amino-2-thiourea) is a crystalline, white solid with molecular weight 91.15 and melting temperature 180–184°C and is soluble in water.

TSC could be considered as derivative of thiourea, where a hydrogen atom of an NH_2 group is substituted with an amino group. Owing to their chemical functions, such as (>C=S, —NH_2, —NH—, etc., TSC compounds could also be effective as antioxidants in stabilization of polymers against thermal oxidation.[29]

Resin preparation

SPI powder was mixed with 10 times (by weight of SPI) distilled, deionized water containing different concentrations of TSC (0, 5, 10, and 20 mass/mass% dry weight of SPI) with constant stirring. The solution was continuously stirred for 6 h to increase the homogeneity; the slurry was allowed to stand for 18–24 h. The pH of the solution was adjusted to 4.5, the isoelectric point of the protein, by adding propionic acid drop by drop while stirring. The slurry was centrifuged to remove excess water (Sorvall Superspeed RC2-B; 4541 g, 10 min) and the precipitated residue was dried for 24 h in a convection oven at 50°C. The dried modified SPI was then milled (Cyclone Sample mill, UDY, Fort Collins, CO) to pass through a 35 mesh sieve.

Characterization

Infrared spectra

Fourier Transform Infrared (FTIR) spectra were recorded with Perkin–Elmer 1720 spectrophotometer using KBr pellets.

Thermogravimetric analysis (TGA)

The modified SPI resin was vacuum dried at room temperature for 18 h at 710 mmHg and then scanned using thermogravimetric analyzer (TGA-2050, TA Instruments, New Castle, DE) from 35 to 800°C at a rate of 10°C/min in N_2 atmosphere. The temperature at which slope of the weight loss versus temperature curve starts to increase was considered as the temperature of initiation of the degradation phenomenon.

Differential scanning calorimetry (DSC)

The modified resin was vacuum dried at room temperature for 120 h at 710 mmHg to eliminate all the free water present. About 15 mg of the resin speci-

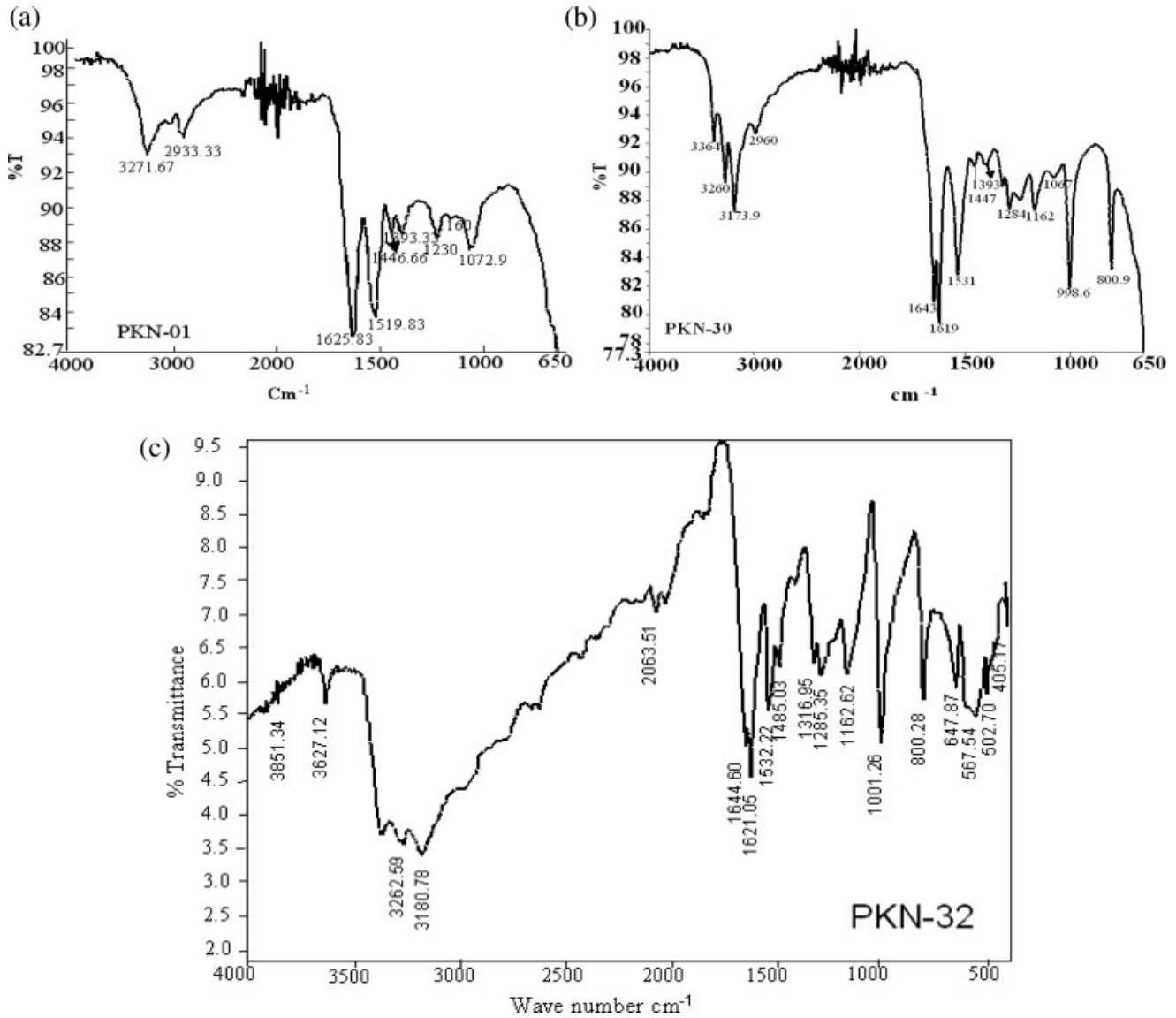

Figure 1 FTIR spectral data of SPI resin modified with (a) TSC-00% (b) TSC-20%, and (c) Pure TSC.

men was compressed in the aluminum standard pans and scanned in duplicate using differential scanning calorimeter (DSC-2920, TA Instruments, New Castle, DE) at a rate of 10°C/min from room temperature (50°C) to 500°C in N_2 atmosphere. The specimen was cooled at a rate of 10°C/min from 500 to 0°C followed by reheating at the rate of 10°C/min.

X-ray diffraction (XRD)

The general area detection diffraction system (GADDS, Bruker-AXS, Madison, WI) was used at 40 kV and 40 mA to study the texture in TSC-modified-SPI resin. The X-ray diffraction patterns of the resin specimens were obtained using a Scintag θ–θ powder diffractometer (PAD X, Scintag, Cupertino, CA) with a solid-state intrinsic germanium detector. The specimens were scanned from 10° to 100° at 2°/min employing the Cu Kα X-ray radiation of 1.5405 Å at 45 kV, and 40 mA. The signal obtained was smoothed using the three-point boxcar function and was analyzed to estimate the degree of crystallinity of the resin. Pure SPI as well as all the modified resin samples were used in powder form for obtaining their X-ray diffraction patterns.

Scanning electron microscopy (SEM)

The microstructure of the modified SPI specimens, containing different concentrations of TSC was characterized using SEM (440, Leica Cambridge, Cambridge, UK). The powdered specimens were placed on the Cambridge standard aluminum specimen mounts (pin type) with double-sided adhesive electrically conductive carbon tape (SPI Supplies,

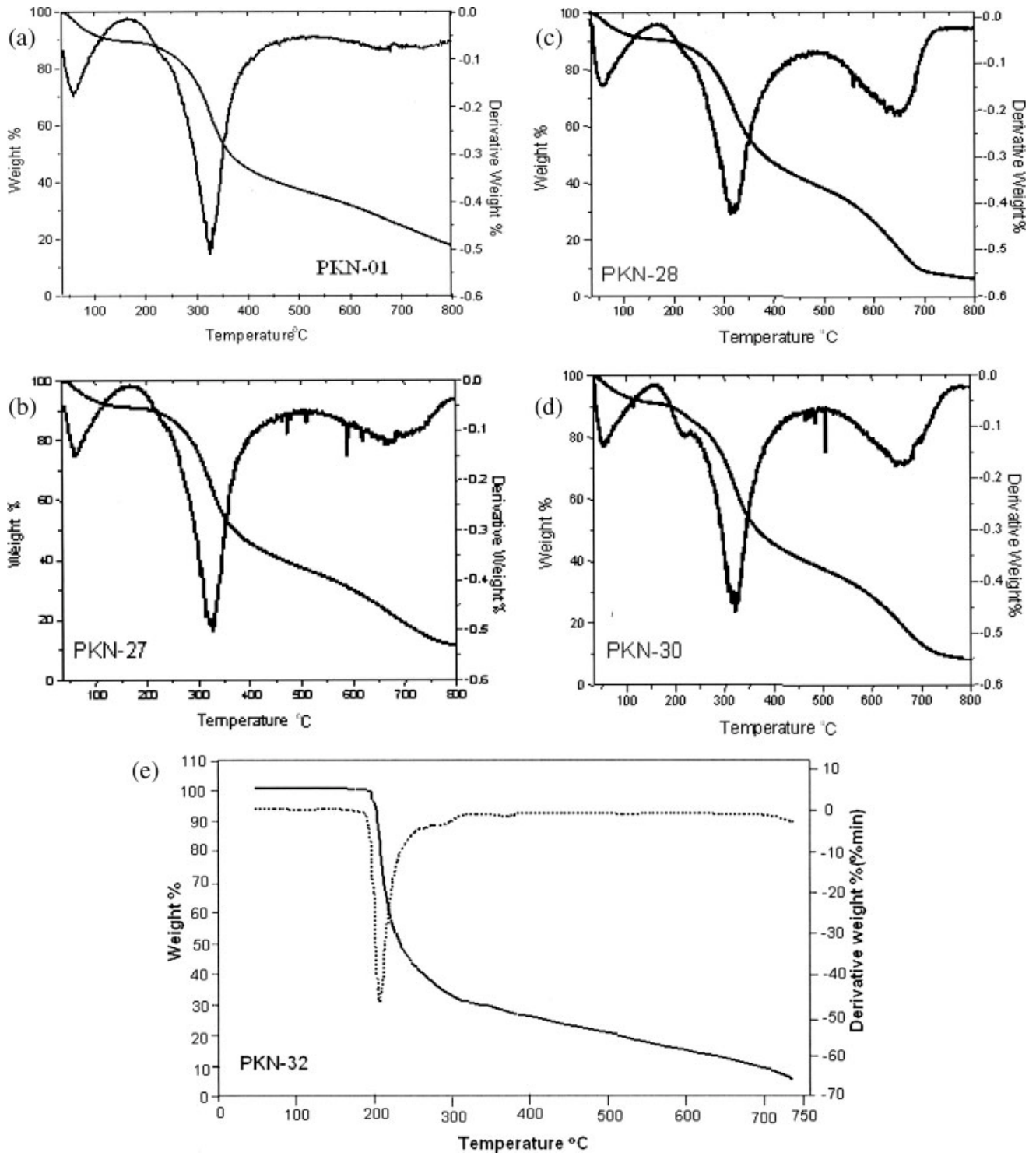

Figure 2 TGA scans of modified SPI with different concentrations of TSC. (a) PKN-01, (b) PKN-27, (c) PKN-28, and (d) PKN-30 with 0, 5, 10, 20%, and (e) Pure TSC.

West Chester, PA). The specimen mounts were then coated with 60% gold and 40% palladium for 30 s with 45 mA current in a sputter coater (Desk II, Denton Vacuum, Moorestown, NJ). The coated specimens were then observed on the SEM using an accelerating voltage of 20 kV at a tilt angle of 30° to observe the microstructure.

Biodegradability test

The biodegradability of modified SPI resin was investigated using aerobic biodegradability procedure (ASTM D 5209-92). The compression molded samples (25.45 mm diameter and 3.0 mm thickness) were broken into smaller pieces and placed in compost

TABLE I
Thermal Decomposition Data of Modified SPI with Thiosemicarbazide in Propionic Acid Medium

Sample code	% of thiosemicarbazide	Mass loss % at various temperatures in °C							
		100	200	300	400	500	600	700	800
PKN-01	00	8	12	25	55	63	68	76	83
PKN-27	05	7	10	23	53	62	70	81	89
PKN-28	10	7	10	25	54	63	74	91	94
PKN-30	20	7	11	27	55	63	72	87	92

devised by us, being prepared as per Lodha and Netravali.[5,30] Within a short period of time the samples displayed excellent growth of bacteria on the surface. The samples were taken out periodically at regular intervals of time, washed thoroughly, pressed with paper towel, dried, and weighed. After about 70 days, the amount of mass left was almost negligible indicating complete degradation of modified SPI.

RESULTS AND DISCUSSION

FTIR analysis of the resin

The FTIR spectrum of the neat SPI [TSC-0%] [Fig. 1(a)] was studied. The absorption bands related to C—O stretching at 1630 cm^{-1} (1625.83 cm^{-1}), *N*—H bending at 1530 cm^{-1} (1519.83 cm^{-1}), and C—H deformation at 1450 cm^{-1} (1446.66 cm^{-1}) were observed. The absorption band at 1230 cm^{-1} is attributed to the C—N stretching and *N*—H bending vibrations. The band at 1100 cm^{-1} is due to the out-of-the plane C—H bending.

In PKN-30, the broad absorption band observed in the range 3600–3000 (3364 cm^{-1}) is attributed to the free and bounded O—H and *N*—H groups. The O—H and *N*—H groups in SPI and the O—H in absorbed water forms inter- and intramolecular hydrogen bonding with the C—O moiety of the amino acids (peptide and carboxyl groups) in the protein structure. The characteristic C—H stretching of the CH_2 and CH_3 groups of saturated structures is observed in the range 2980–2850 cm^{-1} (2960 cm^{-1}). FTIR scan of the modified SPI resin PKN-30, [Fig. 1(b)] shows an extra absorption band at 3364 cm^{-1}, which is due to the *N*—H stretching of the primary amino group. The band around 1646 cm^{-1} is due to the secondary *N*—H group. The band around 1283 cm^{-1} is due to C—N stretching and that of 1066 cm^{-1} is due to C—S stretching. These bands are absent in case of unmodified sample (PKN-01). The FTIR spectra clearly indicate that, TSC has not been crosslinked with SPI and acts as a filler.

The FTIR spectrum of the pure TSC [PKN-32 in Fig. 1(c)] has been taken. A peak at 3262 cm^{-1} indicates *N*—H stretching of the primary amino group, band around 1621 cm^{-1} is due to the secondary *N*—H group and the band around 1285 cm^{-1} is due to C—N stretching and that of 1162 cm^{-1} is due to the C—S band of TSC.[31–33]

Thermal degradation studies

The thermogram of each of the TSC-modified SPI could be dissected into four steps [Fig. 2(a–d)]. For example, in case of sample PKN-30 (Table I), the first break takes place around 125°C having weight loss about 7%, the second break takes place around 187°C having weight loss of about 11%, the third break takes place between 188 and 350°C having weight loss about 50% and the fourth break takes place around 800°C having weight loss around 92%. This can be explained by considering the complex structure of soy-protein. It is well known that the three-dimensional structure of soy-protein is governed by its primary structure *i.e.*, the sequence of amino acids. Two kinds of covalent bonds are mainly found in proteins: one is the peptide bond between the amino acid residues and the other is the disulfide bond. The other noncovalent bonds present in protein are electrostatic and hydrophobic interactions and the hydrogen bonding.

The first break around 125°C is attributed to the elimination of absorbed water and the dissociation of the quaternary structure of proteins. Further it is well known[4] that, beyond 100°C the protein denatures their subunits and promotes the formation of protein aggregates via electrostatic, hydrophobic, and disulfide interchange bonding mechanisms. This has been recently substantiated by Swain et al.[4] It is generally accepted that hydrophobic and disulfide bonding is involved and responsible for protein–protein aggregation caused by heating to temperature above 100°C. Further, during this period, the electrostatic hydrogen bonding is also affected.

The second break between 127°C and 187°C is mainly due to the cleavage of the covalent bonding between the peptide bonds of amino acid residues. During this period 60% of phenyl alanine and tryptophan residues and 80% of tyrosine residue are burnt. Further heating also causes three simultaneous reactions in the structure of soy protein; first, the dissociation of 7S and 11S protein subunits; second, the

TABLE II
Kinetic Parameters of SPI Resins Modified with Thiosemicarbazide

Sample no_steps	Temp. range (°C)	Model	Slope	Intercept	R^2	Activation energy, E (kJ/mol)	Frequency factor
PKN01_1	38–105	B1	−1097.7	8.2249	0.9863	20.10	12508.0
PKN01_2	106–250	B1	−849.4	7.1167	0.9509	15.56	3195.5
PKN01_3	251–353	B1	−2325.5	9.4523	0.9708	42.59	90425.3
PKN01_4	354–800	B1	−1244.6	7.3215	0.9740	22.80	5746.4
PKN27_1	41–120	B1	−1044.5	8.0231	0.9785	19.13	9727.0
PKN27_2	121–220	B1	−1035.0	7.5750	0.9385	18.96	6157.2
PKN27_3	221–358	B1	−1892.3	8.7365	0.9796	34.66	35964.6
PKN27_4	359–799	B1	−1346.9	7.4300	0.9756	24.67	6931.0
PKN28_1	33–129	B1	−961.8	7.7816	0.9724	17.62	7034.8
PKN28_2	131–202	B1	−1310.9	8.2178	0.9530	24.01	14831.4
PKN28_3	203–363	B1	−1685.7	8.3956	0.9853	30.87	22783.9
PKN28_4	365–795	B1	−1494.3	7.6065	0.9815	27.37	9174.5
PKN30_1	35–125	B1	−893.4	7.6084	0.9877	16.36	5495.8
PKN30_2	127–187	B1	−1444.5	8.5723	0.9488	26.46	23295.5
PKN30_3	188–350	B1	−1490.8	8.0894	0.9732	27.30	14834.8
PKN30_4	353–802	P1	−1145.4	7.1377	0.9813	20.98	4400.3

unfolding of the subunit secondary structure; and third, the reassociation of denatured subunits via disulfide, hydrophobic, electrostatic, and other important bonding forces. The third break between 188 and 350°C is probably due to cleavage of *S*—S, O—N and O—O linkages of the protein molecule. The fourth break between 353 and 800°C is attributed to complete decomposition of protein molecule forming various gases like CO, CO_2, NH_3, H_2S, and other gases. Beyond 800°C only the char residue remains.

TGA of pure TSC [PKN-32 in Fig. 2(e)] has been compared with the TGA of PKN-30 (SPI modified with 20%TSC). A perusal of TGA indicates that 10% degradation takes place at about 200°C. After 200°C, the rate of degradation is very fast and around 70–75% degradation takes place at about 350°C. This result indicates that, since the molecular mass of TSC is very small, the degradation is very fast.

A perusal of the degradation pattern of the modified TSC–SPI indicates very interesting phenomenon.

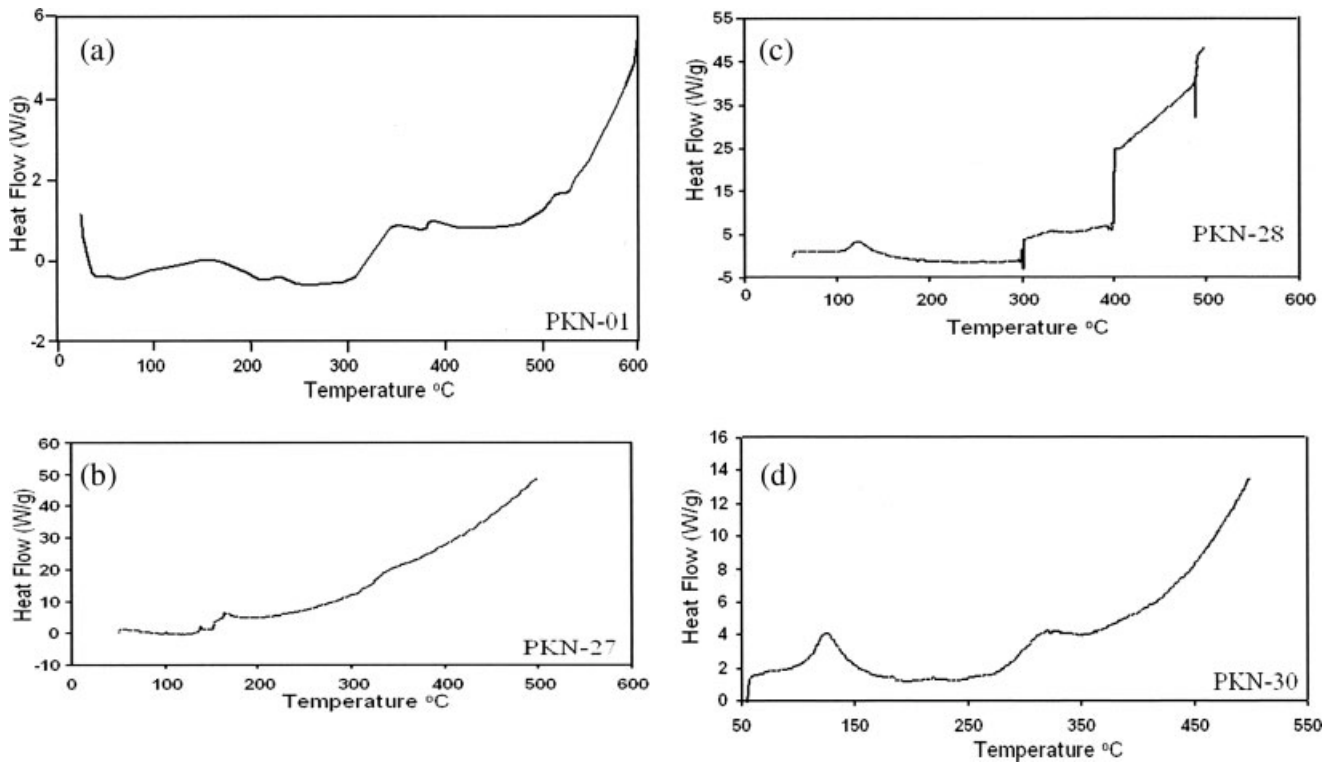

Figure 3 DSC scans of SPI resin modified with TSC: (a) PKN-01, (b) PKN-27, (c) PKN-28, and (d) PKN-30.

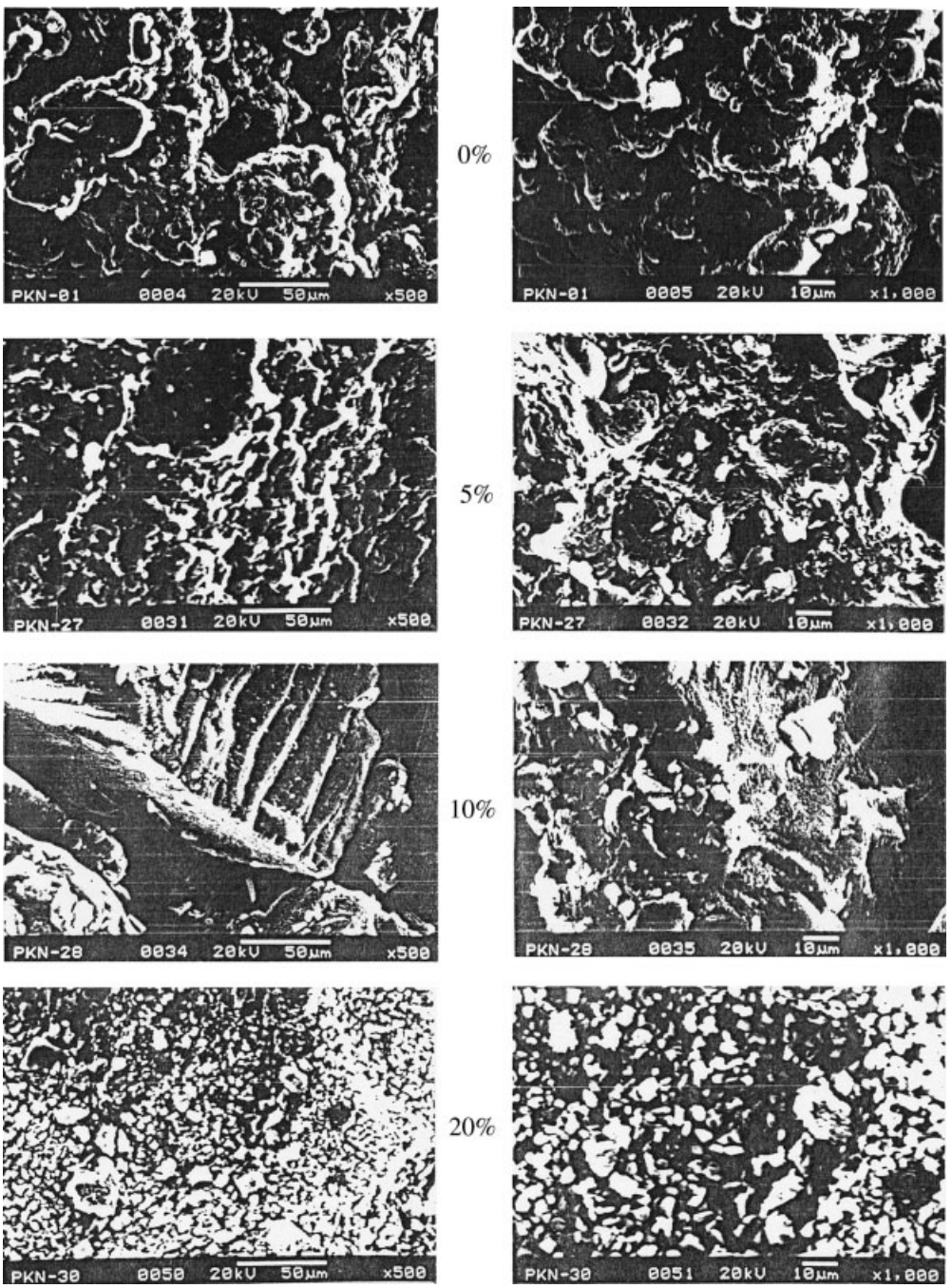

Figure 4 SEM photomicrographs of SPI resins modified with different concentrations of TSC (0, 5, 10, and 20%).

All the resins degraded in four steps as monitored by 'B1' model. Comparing the degradation of the neat sample (PKN-01) with the SPI sample modified with 5% TSC (PKN-27), it is ascertained that the degradation pattern in both cases is almost the same. Comparing the activation energy values, it is noticed that, the second step of degradation is much faster than the first step.

But the thermal degradation pattern changes completely with increase in temperature. The third step becomes slower than the fourth step as is evident from the values of the activation energy (Table II). This may be due to the entanglement of TSC into the matrix of the protein for which the third and fourth steps become slower. In the final step, most of the TSC must have been decomposed, as a result of which, the matrix of the protein must be free and the process of decomposition is fast eliminating gases like CO_2, NO, NO_2, and SO_2, etc. It has been pointed out by Moharram and Abd-El-Nour[31] that, the protein structure changes dramatically with heating. Sometimes, the folding and unfolding of the

TABLE III
Degree of Crystallinity of SPI Resin Modified with Thiosemicarbazide

Sample	Composition	2θ	Peaks	Xcr	Average Xcr
	Neat SPI	21.85	1	0.27975	
	TSC-0%	38.75	2	0.01385	
		44.75	3	0.11749	
		72.4	4	0.23826	
PKN-01		88.15	5	0.12354	0.154578
	TSC-10%	19.1	1	0.12312	
		24.65	2	0.05064	
		28.25	3	0.09227	
		38.45	4	0.13226	
		44.75	5	0.1501	
		65.15	6	0.15636	
PKN-28		72.5	7	0.17006	0.124973
	TSC-20%	18.95	1	0.16272	
		24.6	2	0.16907	
		28.2	3	0.2959	
		35.5	4	0.12605	
		38.5	5	0.12689	
		44.8	6	0.15075	
		65.25	7	0.13407	
PKN-30		78.35	8	0.07095	0.153383

structure also takes place. The reaction mechanism of the degradation involved, firstly, the scission of the weakest C—N, C(O)—NH, CO—NH_2, and NH_2 bonds, which were present in various active groups in the protein.

DSC

Four SPI samples including the neat SPI were monitored for DSC. The DSC scan of pure SPI resin (without TSC) did not show any significant endothermic or exothermic transitions [Fig. 3(a)]. The DSC scan of TSC modified resin did not show any second order glass transition temperature (T_g) or endothermic transitions such as denaturation temperature (T_d). There is no sharp onset of a melting point and no visible temperature of crystallization of the TSC-modified products. The modified products can be considered as amorphous polymers that are not arranged in ordered crystals, but randomly strewn together in the formation of solid state.[27] Combining all DSC heating curves provided a mean glass transition temperature of 163, 123, and 125°C and melting temperature of 341, 302, and 320°C were obtained for PKN-27, PKN-28, and PKN-30 [Fig. 3(b–d)] respectively. As the concentration of the modifier increases, the T_g and T_m decrease accordingly, which is expected considering the action of the modifier. An increasing tendency along the increased concentration (20%) of modifier is observed.

SEM

It is well known that at relatively low concentrations (2–5%), TSC may serve as a good plasticizer, which increases the plastic strain at break.[28] At very high concentrations, TSC may act as a good filler, which increases the plastic thickness. Nearly linear elastic deformation and brittle fracture behaviors were observed for the unmodified SPI plastics (Fig. 4). The plastics from TSC-modified SPI showed great deviation from linear deformation. All plastic samples modified with different concentrations of TSC displayed rough and fluctuant fracture surfaces Therefore, both deformation behavior and fracture surface indicated that plastics/resins from TSC-modified SPI were tougher than that from the unmodified SPI. As the concentration of TSC increases, the surface of the plastics become more homogeneous indicating that at higher TSC concentration it acts as a good filler.

XRD studies

The X-ray diffraction pattern of the unmodified and modified SPI gave very strong and distinct peaks 19, 21, 28, 35, 38, 44, 65, 72, and 88 at 2θ for PKN-1, PKN-28, and PKN-30 respectively. The values of XCr are furnished in Table III. A perusal of the XCr values indicates that the degree of crystallinity varies from 0.12 to 0.15. By increasing the modifier concentration, the values of XCr first decreases in the initial stage, but with further increase, it increases. Further it can be ascertained that the resin remains mostly in the amorphous state without being a very ordered structure.

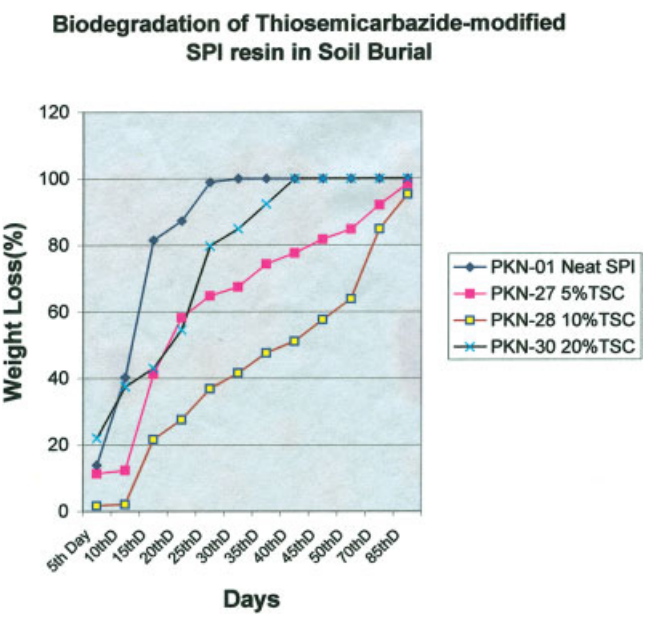

Figure 5 Biodegradation of modified SPI resin sheets in soil burial (% weight loss). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Biodegradability test

The biodegradability of modified SPI resin was investigated using aerobic biodegradability procedure (ASTM D 5209-92). Compression molded samples (25.45 mm diameter and 3.0 mm thickness) were broken into smaller pieces and placed in compost devised by us. Within a short period of time the samples displayed excellent growth of bacteria on the surface. The samples were taken out periodically at regular intervals of time, washed thoroughly, pressed with paper towel, dried, and weighed. The data is represented in Figure 5 taking day's interval and % weight loss with time.[5,30]

CONCLUSIONS

SPI is considered as a potential substitute to petrochemical plastics for the manufacture of plastics because it is agro-based, cheap, and biodegradable. Considering the global environmental problem and shortage of petroleum-based plastics, this is indeed a good candidate in the twenty first century for the production of environmental-friendly plastics. Soy protein alone can not be used as plastic since it is rigid and brittle. A plasticizer or modifier is required for molding the plastic for commercial use. At lower concentration, TSC is a good modifier to improve the properties of SPI. The FTIR spectra of the modified resin shows that SPI is not cross-linked with TSC, rather it acts as a modifier. A computerized LOTUS package analysis method, developed by us, is used for monitoring the degradation mechanism of the resin. The degradation of the resin at different temperature range has been evaluated and the kinetic parameters have been calculated using different equations. Based on the values of energy of activation, the degradation pattern has been ascertained. From the DSC thermogram, glass transition temperature (T_g) has been calculated for the modified resin. All plastic samples modified with different concentration of the modifier displayed fluctuant fractured surfaces. From the X-ray diffraction pattern of the modified SPI, it has been ascertained that resins remain mostly in an amorphous state. The biodegradability of the modified SPI was studied using two different methods. It was found that they degrade within reasonable time period.

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